

An acid bath for the electrodeposition of glossy gold and
gold alloy layers and a gloss additive for same

Description:

The invention provides an acid bath for the
5 electrodeposition of glossy gold and gold alloy layers and
a gloss additive for same.

Electroplating gold baths usually contain gold and
optionally one or more alloy elements in dissolved form.

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10 These types of electrolytes are mainly based on gold
cyanide complexes. It is necessary to adjust these
electrolytes to a weakly to moderately acid pH by using
inorganic and/or organic acids and buffer salts.

15 So that glossy gold or gold alloy layers are deposited
from such baths, these usually contain specific inorganic
or organic compounds as so-called "gloss additives".

A typical, very frequently used gloss additive is, as
described for example in DE 23 55 581, the compound
pyridine-3-sulfonic acid.

20 These types of additive shift or extend the working range
which can be used, that is the range of current densities
within which a glossy gold coating is deposited, in the
direction of higher current densities. There again, the
use of higher current densities enables deposition to
proceed at a greater rate.

25 On the other hand, the working range of these types of
gold baths also depends on the pH of the electrolytes.
This means that if the pH is higher the working range
(current density range which can be used) becomes
narrower, but at the same time the current efficiency, and
30 thus the rate of deposition, is increased.

Therefore, the object of the invention was to optimise the working conditions and deposition performance in these types of gold baths in such a way that on the one hand a maximum current density/working range is produced with the smallest possible negative effect when the pH is changed and on the other hand a maximum current efficiency and rate of deposition is achieved.

Surprisingly, it has now been found that this can be achieved if at least one compound of the general formula I is added as a further gloss additive to these types of baths for deposition of glossy gold layers,



wherein

m is the number 3 or 4, and

R represents a straight-chain or branched or cyclic alkyl group with up to 20 carbon atoms and, in the event that $m = 4$, also an aryl or heteroaryl group with up to 10 carbon atoms, which may be optionally substituted once or several times with straight-chain or branched alkyl groups with 1 to 14 carbon atoms.

Thus, the invention provides an acid bath for the electrodeposition of glossy gold and gold alloy layers containing gold and optionally one or more alloy elements in dissolved form and also at least one organic compound as a gloss additive, characterised in that the bath contains, as a further gloss additive, at least one compound of the general formula



wherein

3

m is the number 3 or 4, and

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10 Gloss additives in accordance with formula I are chosen from the classes consisting of alkyl sulfonates and alkyl, aryl or heteroaryl sulfates. In formula I, if m is the number 3 or 4 then R represents a straight-chain or branched or cyclic alkyl group with up to 20 carbon atoms.
15 If m is the number 4 than R may also represent an aryl or heteroaryl group with up to 10 carbon atoms, wherein these may be substituted once or several times with straight-chain or branched alkyl groups with 1 to 14 carbon atoms.

20 Compounds of the formula I are known per se and are either commercially available or can easily be prepared by standard processes.

These compounds are sufficiently soluble in water and are compatible with the electrodeposition bath. The compounds have surfactant properties, wherein the corresponding
25 effect is reduced when the total number of carbon atoms is less than 4 and generally sufficient solubility is no longer exhibited when the total number of carbon atoms is greater than 20.

30 Preferred gloss additives are compounds of the formula I in which R represents straight-chain or branched or cyclic alkyl groups with 5 to 12 carbon atoms and in particular for branched alkyl groups with 6 to 10 carbon atoms.

Typical gloss additives according to the invention are

pentyl sulfonate	pentyl sulfate
hexyl sulfonate	hexyl sulfate
heptyl sulfonate	heptyl sulfate
5 octyl sulfonate	octyl sulfate
nonyl sulfonate	nonyl sulfate
decyl sulfonate	decyl sulfate
dodecyl sulfonate	dodecyl sulfate
cyclohexyl sulfonate	cyclohexyl sulfate

10 and their isomers.

These compounds may also be present in the form of their salts.

15 Branched and short-chain compounds are particularly suitable due to their low tendency to pronounced foam production, in particular in processes and plant in which severe foam production could cause problems, e.g. in the case of air-stirred electrolytes, when processing in drums, in plants for high-speed deposition (spray plants) and in plants for selective deposition such as e.g.
20 dipping cells.

The use of the further gloss additive according to the invention in acid baths for the electrodeposition of glossy gold and gold alloy layers expediently takes place in the concentration range from 0.01 to 10 g/l. Baths
25 according to the invention which contain the gloss additive in accordance with formula I at a concentration of 0.1 to 5 g/l are particularly advantageous.

Due to the use according to the invention of compounds of compounds (sic) of the formula I as a further gloss
30 additive in electrodeposition gold baths with an otherwise conventional composition, the current density/working

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range which can be used is considerably extended in an unexpected manner and at the same time the current efficiency and the deposition performance are sometimes drastically increased.

5 To prepare gold baths according to the invention, many commonly used and commercially available weakly acidic gold baths may be used as the starting composition to which a corresponding amount of the compound of the formula I is added. The qualitative and quantitative
10 composition of these types of gold baths is extremely well-known to a person skilled in the art from literature and from practice and therefore does not require a detailed explanation. In every case, these contain gold in dissolved form, obtained from gold salts or gold complex
15 salts, wherein mainly gold cyanide complexes are used. Furthermore, the baths may contain alloy elements in the form of dissolved salts or complex salts. Furthermore, the baths contain inorganic and/or organic acids, corresponding salts and optionally buffer and supporting
20 electrolytes in order to adjust the pH and the conductivity. In order to deposit glossy, smooth gold layers, organic compounds are generally contained therein, these mostly having surfactant properties and acting as a gloss-producer. A typical and well-proven gloss-producer
25 of this type is pyridine-3-sulfonic acid.

Furthermore, the following compounds and their salts and derivatives are also suitable as conventional gloss additives:

nicotinic acid

30 nicotinamide

3-(3-pyridyl)-acrylic acid

3-(4-imidazolyl)-acrylic acid

3-pyridylhydroxymethanesulfonic acid

pyridine

picoline

quinolinesulfonic acid

5 3-aminopyridine

2,3-diaminopyridine

2,3-di-(2-pyridyl)-pyrazine

2-(pyridyl)-4-ethansulfonic acid

1-(3-sulfopropyl)-pyridinium betaine

10 1-(3-sulfopropyl)-isoquinolinium betaine

Electrodeposition gold baths according to the invention typically contain about

0.1 - 50 g/l of gold as a gold cyanide complex

15 0 - 50 g/l of alloy elements such as iron, cobalt, nickel, indium, silver, copper, cadmium, tin, zinc, bismuth, arsenic, antimony as a salt or complex salt

20 10- 200 g/l of citric acid/citrate as a buffer and/or supporting electrolyte

0.1 - 10 g/l of pyridine-3-sulfonic acid as gloss-producer

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0.1 - 5 g/l of a compound of the formula I as a
further gloss additive according to
the invention,

wherein the pH of the bath is adjusted to 3 to 6,
preferably 4 to 5.

Use of the gloss additive according to the invention
produces a number of practical advantages. Thus, under
otherwise unchanged conditions, the deposition performance
can be clearly increased. Due to the wider working range,
fine adjustment of the mode of operation is less critical,
wherein the risk of defective deposition is greatly
reduced.

However, a higher pH may also be used with an unchanged
working range. The deposition performance can also be
increased in this way.

Alternatively, however, a smaller gold concentration may
be used while retaining the same deposition performance.
The advantages associated with this move are the smaller
losses due to electrolytes being carried over by adhering
to the goods and the smaller amount of capital which is
tied up.

Example 1:

A working range of up to 3 A/dm² is produced with a cell
current of 2 A in a coating cell which contains a
gold/cobalt electrolyte containing

10 g/l of gold in the form of potassium gold(I)
cyanide

0.5 g of cobalt as cobalt sulfate

100 g/l of citric acid

3 g/l of pyridine-3-sulfonic acid.

adjusted to pH 4.2 with potassium hydroxide,

(trial conditions: platinised titanium anode, temperature 50°C, time 2 min, agitated at 500 rpm with a 25 mm magnetic stirring rod). The current efficiency at 3 A/dm² is 48 %; the rate of deposition is 0.98 µm/min.

By adding 1 g/l of nonyl sulfate, the maximum current density which can be used is increased to more than 5 A/dm². This corresponds to extending the working range by more than 66 %.

If the pH is then raised to 4.4, a working range of up to 4 A/dm² is produced; the deposition performance is 1.05 µm/min.

At a pH of 4.6 the working range extends up to 3 A/dm² and a rate of deposition of 1.15 µm/min is produced.

Example 2:

A maximum current density of 3 A/dm² is achieved in a gold/nickel electrolyte containing

10 g/l of gold in the form of potassium gold(I) cyanide

0.7 g of nickel in the form of nickel sulfate

100 g/l of citric acid

3 g/l of pyridine-3-sulfonic acid,

adjusted to pH 4.2 with potassium hydroxide,

on pre-nickel-coated sheets with the dimensions 25 x 40 mm (trial conditions: 1 litre glass beaker, platinised titanium anode, bath agitated at 200 rpm using a 60 mm magnetic stirring rod, goods moved at 5 cm/s). The cathodic current efficiency at 3 A/dm² is 52 % and the rate of deposition is 1.0 µm/min.

By adding 0.5 g/l of decyl sulfate, the maximum current density which can be used is increased to more than 7 A/dm². At 7 A/dm² the current efficiency is still 26 %, the deposition performance increases to 1.18 µm/min. This corresponds to increasing the rate by 18 %.

Example 3:

A maximum current density of 5 A/dm² is achieved in a gold/iron electrolyte containing

- 10 10 g/l of gold in the form of potassium gold(I) cyanide
- 0.05 g of iron as iron (III) citrate
- 100 g/l of citric acid
- 3 g/l of pyridine-3-sulfonic acid,
- adjusted to pH 4.2 with potassium hydroxide,
- 15 on sheets with the dimensions 25 x 40 mm (for conditions, see example 2). The cathodic current efficiency is 31 % and the rate of deposition is 1.0 µm/min.

- By adding 4 g/l of hexyl sulfate the maximum current density which can be used is increased to more than
- 20 6 A/dm². At 6 A/dm² the current efficiency is still 30 %; the deposition performance increases to 1.16 µm/min. This corresponds to increasing the rate by 16 %.

Example 4:

- 25 A working range of up to 5 A/dm² is produced in a coating cell with a cell current of 2 A in a gold/cobalt electrolyte containing

- 10 g/l of gold in the form of potassium gold(I) cyanide
- 30 0.5 g of cobalt as cobalt sulfate
- 100 g/l of citric acid

1 g/l 3-(3-pyridyl)-acrylic acid,
adjusted to pH 4.2 with potassium hydroxide,

(trial conditions: platinised titanium anode, temperature
50°C, time 2 min, agitated at 500 rpm with a 25 mm⁻
5 magnetic stirring rod). The current efficiency at 5 A/dm²
is 26 %; the rate of deposition is 0.83 µm/min.

By adding 1.5 g/l of octyl sulfate the maximum current
density which can be used is increased to more than
8 A/dm². At 8 A/dm² the current efficiency is still 19 %;
10 the deposition performance increases to 1.0 µm/min.

Example 5:

In the gold/cobalt electrolyte from example 1, the maximum
current density which can be used is increased to more
15 than 5 A/dm² by adding 1 g/l of hexyl sulfonate. At 5 A/dm²
the current efficiency is 35.1 %, the deposition
performance is increased to 1.13 µm/min. This corresponds
to increasing the rate by 15 %.

20 Example 6:

In the gold/cobalt electrolyte from example 1, the maximum
current density which can be used is increased to more
than 7 A/dm² by adding 1 g/l of octyl sulfonate. At 7 A/dm²
the current efficiency is 26.2 %, the deposition
25 performance increases to 1.18 µm/min. This corresponds to
increasing the rate by 20 %.

Example 7: Comparison example

In a gold/cobalt electrolyte (see example 1) consisting of

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10 g/l of gold in the form of potassium gold(I)
cyanide

0.5 g of cobalt as cobalt sulfate

100 g/l of citric acid,

5 adjusted to pH 4.2 with potassium hydroxide,

and using the trial conditions in example 1, the effect on
the working range and the rate of deposition was
determined when adding only octyl sulfate, only pyridine-
3-sulfonic acid and both substances together as a gloss
10 additive. The results are given in table 1.

The combination of the two substances greatly extends the
working range and causes a considerable increase in the
rate of deposition.

Table 1:

Octyl sulfate	Pyridine-3- sulfonic acid	Working range (gloss) up to	Rate of deposition
-	-	2 A/dm ²	0.63 µm/min
2 g/l	-	2 A/dm ²	0.65 µm/min
-	3 g/l	3 A/dm ²	0.98 µm/min
2 g/l	3 g/l	5 A/dm ²	1.12 µm/min